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Synthesis and characterization of NiO nanoflower for dispersive micro solid phase extraction of zinc from water and food samples

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ABSTRACT

This study introduces a dispersive micro solid phase extraction (DμSPE) method utilizing NiO nanoflowers for the analysis of zinc in food, environmental, and wastewater samples, employing Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES). The synthesized NiO nanoflower-like nanoparticle was characterized through Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). Additionally, various parameters including pH, sample volume, adsorbent quantity, and extraction time were investigated to optimize the NiO nanoflower-based SPME (NiO nanoflower-SPME) method. The analytical performance metrics, specifically the limit of detection (LOD), limit of quantification (LOQ), and relative standard deviation (RSD), were determined to be 0.77 μg L^{-1}, 2.56 μg L^{-1}, and 3.9 %, respectively. Furthermore, addition-recovery studies conducted on real samples, along with analyses of standard reference materials, were performed to validate the accuracy of the method. With these results, it was concluded that the NiO nanoflower-SPME method is crucial for the analysis of zinc in real samples due to the fact that the complex matrix environment complicates the analysis.

1. Introduction

Most elements present in the environment are naturally occurring, typically existing in dissolved form in water bodies, where they may precipitate onto sediment layers. Additionally, trace elements are often introduced into rivers and groundwater as a consequence of anthropogenic activities, leading to potential toxic effects and contributing to environmental pollution. Conversely, some of these elements are essential for living organisms, highlighting the dual nature of their presence in the ecosystem (El Hosry et al., 2023).

Zinc is metabolically significant due to its critical role in the biological processes of humans, animals, and plants. It serves various functions, particularly as a co-factor in numerous enzymatic activities. However, excessive zinc intake can lead to adverse health effects, including oxidative stress, developmental and reproductive complications, impaired immune function, and difficulties in weight gain. Given its metabolic significance and impact on health, it is essential to conduct analyses of samples containing zinc (Escudero et al., 2010; Salgueiro et al., 2000). The upper tolerable intake level of Zinc according to US Food and Nutrition Board (FNB) has been reported as 40 mg/d for adults older than 19 years (Nriagu, 2007).

The direct determination of trace metals including zinc in environmental water and food samples using techniques such as flame atomic absorption spectrometry (FAAS) (Soylak et al. 2007; Soylak and Kizil, 2011; Carletto et al., 2008), inductively coupled plasma optical emission spectroscopy (ICP-OES) (Suvardhan et al., 2007), electrothermal atomization atomic absorption spectroscopy (ETAAS) (Kiptoo et al., 2008) or inductively coupled plasma mass spectrometry (ICP-MS) (Komjarova

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and Blust, 2006) can be challenging. This difficulty arises from the trace concentrations typically present in these samples, as well as potential interference from matrix components. Therefore, a pre-concentration and/or separation process is necessary. In order to overcome all these extraction challenges, solid phase and liquid phase microextraction methods have been developed. These methods can be applied as solid phase extraction (Jalili et al., 2020; Cherniakova et al., 2024; Yagmuroglu, 2025; Sakiyan Ates et al., 2025).

Dispersive micro solid phase extraction (DμSPE) is an innovative extraction method used for the extraction of different compounds such as heavy metals, polyaromatic hydrocarbons, pesticides, aflatoxins and pharmaceuticals (Ibrahim et al., 2012; Soylak and Ercan, 2009). In the DμSPE method, sorbent dispersion is done with the help of vortex mixer or a mechanical shaker. The analytes are then eluted with a suitable solvent and used in the next analysis step. The efficiency of a DμSPE is closely related to the structure of the sorbent used (Kole et al., 2011). The main parameters of this efficiency are the interactions of the analytes with the sorbent, adsorption capacity, porosity and functional groups. Different particles including graphene (Ferrone et al., 2020), graphene oxide (GO) (Niu et al., 2018), metal organic frameworks (Wang and Ye, 2017), covalent organic frameworks (Gao, et al., 2019), magnetic nanoparticles (Karami-Osboo et al., 2022) have been used in DμSPE considering these parameters.

Nanoflowers, which are flower-shaped nanocrystalline structures are located between different nanoparticle systems with a nanoscale range of 100–500 nm. They have various applications areas such as removal of heavy metals in water, detection of pathogens in foods as biosensors, and dye removal (Shende et al., 2018). Morphologically, they have a higher surface/volume ratio than spherical nanoparticles with their three-dimensional leafy structures and are therefore more efficient structures (Lee et al., 2015). Metal containing nanoflowers are classified according to their size and the structure of the bound metal ions (Shende et al., 2018). Recent advancements in nanotechnology have suggested that synthesizing nanoparticles through biological methods, utilizing plant extracts and microorganisms, represents an environmentally friendly alternative. The photocatalytic oxidation method, which employs semiconductors as catalysts, has emerged as an environmentally friendly approach for various applications, including water purification, air purification, and soil remediation (Han et al., 2023)

Nickel oxide (NiO) is a significant inorganic nanoflower-like nanoparticle that has extensive applications in various fields, including electrochromic films, p-type transparent conductive films, smart windows, electrochemical supercapacitors, the negative electrode in lithium-ion batteries, adsorption, extraction, and as a catalyst, among others (Soylak et al., 2024; Munkaila et al., 2021; Li et al., 2015). Nickel oxide has a diverse array of applications owing to its high thermal stability, as well as its favorable magnetic and electrical properties (Zhang and Zeng et al., 2017; Paul et al., 2023).

In this study, we developed a DμSPE method utilizing NiO nanoflowers (designated as NiO nanoflower- DμSPE) for the analysis of zinc ions. To achieve this, a nanoflower-structured hybrid material was synthesized and employed for the separation and determination of zinc in water and food samples. The qualitative and quantitative analysis of zinc in the prepared samples was conducted using the ICP-OES.

2. Experimental

2.1. Reagents

All chemicals and reagents utilized in this study were of the highest purity available. Ultrapure water, obtained from a Mp Minipure Dest water purification system (Ankara, Türkiye), was employed consistently throughout the experiments. The stock solutions of Zn were prepared by dilution of their stock solutions (1000 mg L^{-1}) obtained from the VHG Labs, Inc., Manchester, New Hampshire, USA. Calibration solutions were prepared fresh daily by serial dilution of a 1000 mg L^{-1}stock solution (VHG Labs, USA) prepared in HNO_3. Suprapure grade nitric acid (HNO_3, %65) was from Merck (Darmstadt, Germany). Sodium phosphate monobasic dihydrate ($NaH_2PO_4.2H_2O$) was purchased from Carlo Erba Reagents, France. Disodium hydrogen phosphate heptahydrate ($Na_2HPO_4.7H_2O$) was also obtained from Sigma Aldrich (Darmstadt, Germany).

2.2. Synthesis process of NiO nanoflower

All chemicals for the synthesis of NiO nanoflower were used directly with analytical purity. A mixture of 0.1 mmol of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6\ H_2O$) and 0.3 mmol of ammonium fluoride (NH_4F) was prepared, combined with 40 mL of ethylene glycol (EG, 99.5 wt%) and 40 mL of deionized water at room temperature. This mixture was then transferred into a 100 mL volume Teflon-lined stainless steel autoclave. The resulting mixture was heated in an oven at 160 °C for 10 h. The homogeneous solution in the autoclave was then cooled at room temperature. The solution that completed the reaction in the autoclave was allowed to cooled down to room temperature. The precipitate formed after the reaction was collected by centrifugation and separated from the mixture. The collected precipitate was washed repeatedly with ethanol and distilled water to remove impurities. Finally, the green precipitates were dried in a vacuum oven at 80 °C for 6 h to obtain the final products (Fig. S5). The synthesized final product was used for analyzing Zn in real samples (Sun et al., 2019).

2.3. Applications

The NiO nanoflower- DμSPE method was employed to analyze zinc content in various real samples, including hazelnuts, spinach, strawberries, and cocoa, under optimized experimental conditions. This approach enabled accurate and reliable determination of zinc levels across these different matrices.

Prior to analysis, it is essential to prepare the samples in a homogeneous liquid form. For this purpose, 4 g each of spinach and strawberry samples were weighed, followed by the addition of 16 mL of 65 % nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2). Simultaneously, 1 g of ground cocoa and hazelnut samples were prepared with the addition of 16 mL of 65 % HNO_3 and 2 mL of H_2O_2. This preparation ensured thorough digestion and uniformity for subsequent analysis. These mixtures were then subjected to microwave-assisted digestion to ensure complete dissolution (400 PSI, 180 C°, 15 min)

The closed container microwave digesting method employed in this study will reduce contamination, limit sample loss of volatile components, and boost efficiency and yield. Because of the increased system pressure, the closed vessel digestion method permits the utilization of temperatures above the boiling point of the acids involved in the digestion. The process of microwave digestion uses the capacity of conducting ions in solids or mobile electric charges in liquids to convert electromagnetic energy into heat. Reactions accelerated by a microwave are quick, safe, economical, and environmentally benign.

Subsequently, 20 mg of NiO nanoflower adsorbent was introduced into each prepared sample. The pH of the solution was adjusted to 7.0 using 1 mL of buffer solution. After completion of the adsorption and desorption processes, the zinc content in the samples was determined using ICP-OES.

2.4. Instrumentation

The distilled water used in analysis and optimization studies was acquired from Nuve brand Water Distiller ND-4. For the production of ultrapure water, the Dest Up model of the MP minipure pure water device was used. Thermomac brand (MIO101002) vortex mixer was utilized to prepare the solutions quickly and easily. XB 220A Precisa model precision balance was used during the preparation of the materials. J.P. Selecta (Spain) brand ultrasonic bath was used for ultrasound-

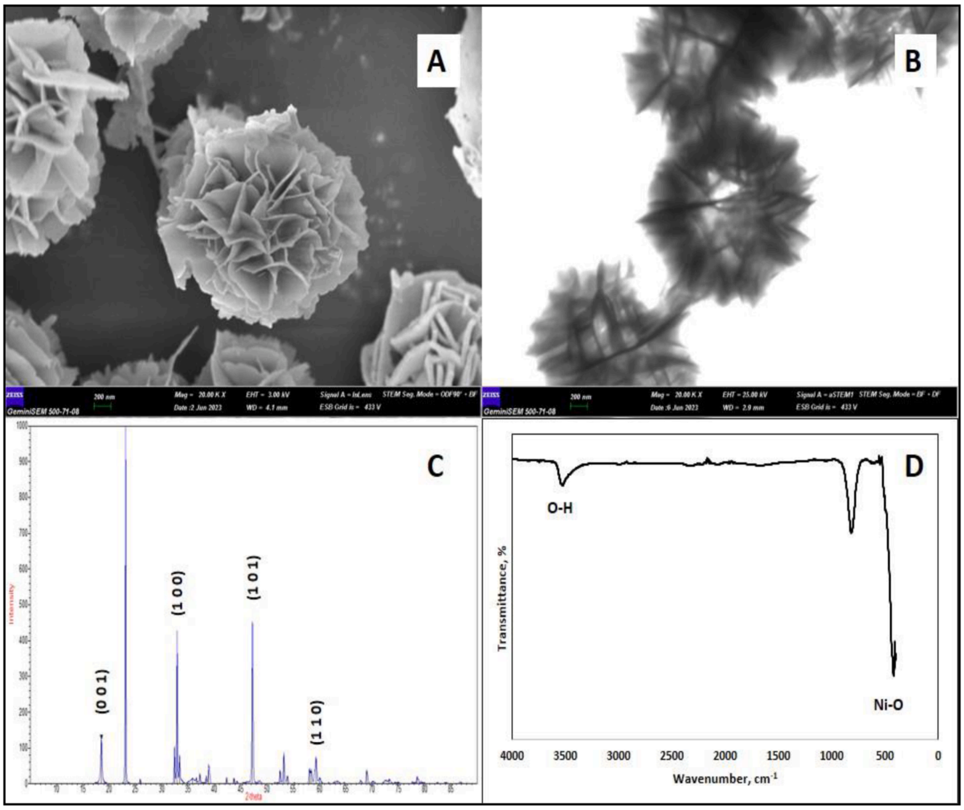

Fig. 1. SEM image (a), STEM image (b), XRD spectra (c), FT-IR spectra (d) of NiO nanoflowers.

powered liquid phase microextraction.

NF 400 Nuve brand (Ankara, Türkiye) centrifuge was utilized for phase separation in adsorbent synthesis and optimization studies prior to analysis. Micro electronic pipettes of 10, 100, 200, 1000 μL and 5–10 mL were used throughout the study (Brand Transferpette S, Germany). For solubilization of solids, a Hanon Instrument Tank Basic microwave reaction system was used (Hanon, China). Furhermore, Perkin Elmer optima 8000 model of ICP-OES was used for the analysis of zinc in food, environmental and waste water samples (PerkinElmer, Inc. Shelton, CT, USA).

2.5. *The DμSPE procedure*

The DμSPE method was optimized for zinc extraction using a 50 mL centrifuge tube. The procedure involved adding 20 mg of adsorbent, 1 mL of pH 7.0 buffer, and 12.5 μg of Zn(II), followed by dilution to 10 mL with water. The mixture was vortexed for 30 s, after which the nanoflowers were separated by centrifugation for 10 min. For desorption, 3 mL of 0.5 mol L^{-1} HNO_3 was used for elution, and the solution was vortexed for 5 min. Subsequently, the eluent and the nanoadsorbent were separated via centrifugation for 10 min. Zinc analysis was performed using ICP-OES, which utilized the upper layer for measurements.

The developed DμSPE method was successfully applied to the analysis of zinc in food and water samples collected from the local markets of Gaziantep, Türkiye, as well as tap and industrial water samples. The detailed experimental procedure is also illustrated in the graphical abstract.

3. Results and discussion

3.1. *Characterization results of NiO nanoflower*

The characterization of the NiO nanoflower was conducted using various analytical techniques, including Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET) technique. SEM and STEM were employed to elucidate the morphology and structural characteristics of the NiO nanoflower composite synthesized via the hydrothermal method.

Fig. 1(a) and 1(b) display the SEM and STEM images of the NiO nanoflower composite, which was reduced to a size of 200 nm at a magnification of 20.000 times. Upon examination of these images, the presence of nano-sized, flower-like structures is distinctly confirmed.

X-Ray Diffraction (XRD) analysis was performed to assess the crystal composition, strain, and grain size of the NiO nanoflower composite materials, as illustrated in Fig. 1(c). The XRD pattern reveals diffraction peaks at 18.6°, 32.6°, 39.0°, and 60.1°. These peaks correspond to literature data (JCPDS No. 14–0117) (Zai et al., 2021; Sun et al., 2019).

In FT-IR analysis (Fig. 1(d)), the O-H vibration of NiO nanoflower composite materials is thought to be responsible for the peak at about 3500 cm^{-1}. The peak around 800 cm^{-1} is probably due to the CO_2 absorbed during synthesis. In addition, it can be seen that well defined Ni–O stretching vibration peak at 421 cm^{-1} (Ceramics International 49.16 (2023): 27230–27246.).

On the other hand, according to BET analysis, the surface area of the nanomaterial was measured as 50.3608 m^2/g. In addition, the average adsorption pore width and desorption pore width were determined to be 126.3927 Å and 126.9493 Å, respectively (Yi et al., 2021).

3.2. *Effect of pH*

To determine the optimal pH for the NiO nanoflower-DμSPE method, a comprehensive study was conducted across neutral, acidic, and basic environments. The developed method was applied to model solutions containing Zn (II) with the pH adjusted to 6.0, 7.0, 8.0, and 9.0. The results demonstrated that the NiO nanoflower-DμSPE method achieved

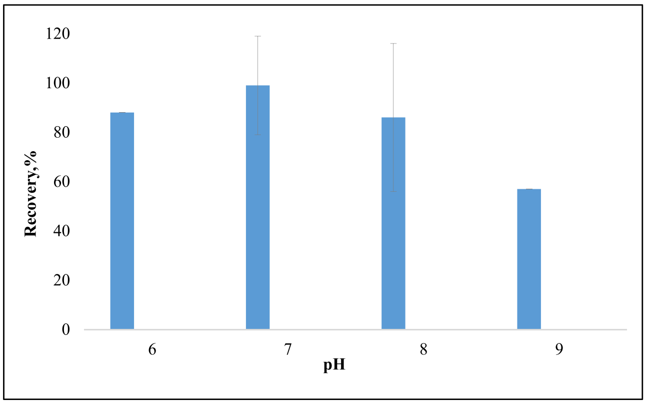

Fig. 2. The optimization of pH (N = 3, eluent volume: 3 mL, adsorbent amount: 20 mg, eluent concentration: 0.5 M).

recovery (Fig. 2). Notably, at pH 7.0 recovery exceeded 95 %. Consequently, further optimization steps and analyses were conducted with the solution pH maintained at 7.0. Because of the competition occurs between proton ions and zinc ions, the recoveries may be reduced. Hence, additionally, zinc ions may precipitate as hydroxides at high basic pH, the extraction efficiency of zinc may be decreased (Abd Wannas et al., 2024; Abdolmohammad-Zadeh et al., 2020).

3.3. Adsorption and desorption time

Another crucial parameter influencing the extraction efficiency of zinc using the NiO nanoflower- DμSPE method is the adsorption/desorption time. Therefore, the effect of adsorption and desorption times ranging from 1 to 7 min on the recovery of zinc were investigated. A mixing time of 5 min was found to be adequate for the quantitative recovery of zinc in both matrices. However, as indicated by the results presented in Fig. S1, extraction efficiency gradually diminished after 5 min due to limitations solvent and adsorbent performance. To summarize, when the results are analyzed, the maximum efficiency was obtained at 5 min for both of them which are equal times.

3.4. Concentration of the eluent

HNO_3 solution was utilized for the desorption of zinc adsorbed by the NiO nanoflower-based micro solid phase extraction method. Elution solutions of HNO_3 were prepared at molar concentrations ranging from 0.5 to 2.0 M to evaluate desorption efficiency. The highest recoveries were achieved with 0.5 M HNO_3, establishing this concentration as optimal. At concentrations above 0.5 M, it is foreseen that potential dissolution of the material may prevent zinc extraction. The outcomes are depicted in Fig. S2.

3.5. Adsorbent amount

To ascertain the optimal quantity of NiO nanoflower for zinc extraction, varying amounts (5–25 mg) were added to the samples. Analysis of the results presented in Fig. S3 indicates that 5 mg of the adsorbent is insufficient for effective zinc extraction. The highest recovery rates were observed at 20 mg of NiO nanoflowers. This amount is significantly lower compared to other adsorbents utilized in zinc extraction (Umaz et al., 2024; Abdolmohammad-Zadeh et al., 2020; Vojoudi et al., 2018) In conclusion, a balance must be between the adsorbent amount and solvent efficacy for optimal extraction performance.

Table 1
Tolerance parameters for foreign ion contaminants for zinc ions analysis (pH: 7.0, N: 3, eluent volume: 3 mL, adsorbent amount: 20 mg, eluent concentration: 0.5 M).

Ion	Concentration, mg L^{-1}	Recovery, %
Al^{3+}	100	90 ± 2
Na^{+}	5000	100 ± 8
Mn^{2+}	5000	98 ± 1
Mg^{2+}	3000	94 ± 1
Pb^{2+}	1000	93 ± 4
Ni^{2+}	4000	90 ± 8
Ag^{+}	2500	94 ± 1
Co^{2+}	10000	94 ± 12
Cd^{2+}	100	91 ± 5

[a] Mean ± standard deviations

3.6. Sample volume

At this stage, a volume studies study was conducted to evaluate the preconcentration factor of the NiO nanoflower-DμSPE method and to determine the optimal sample volume for analysis. Model solutions ranging from 5 to 40 mL were prepared, and separation/preconcentration was performed using the NiO nanoflower-DμSPE method. As illustrated in Fig. S4, recoveries obtained with 20 mg of adsorbent remained above 95 % for sample volumes up to 30 mL. Beyond this volume, the efficiency of the NiO nanoflower-DμSPE method began to decline. Once the optimal sample volume was established, it was calculated as 10 using the equation:

$PF = \frac{\text{Max.sample volume}}{\text{Final volume}} x100$ where the maximum sample volume is 30 mL and the final volume is 3 mL.

3.7. The evaluation of interferences

To enhance the selectivity of the analytical process and achieve more accurate results, it is essential to evaluate the method in different matrix environments. In this study, the influence of several inorganic ions, including Na^+, Al^{3+}, Co^{2+}, Ag^+, Mn^{2+}, Mg^{2+}, Pb^{2+}, and Ni^{2+} (as listed in Table 1), on the determination of 0.25 μg mL^{-1} zinc was investigated. Tolerance concentration values for these ions were calculated, and recovery rates exceeding 90 % across the specified concentration ranges demonstrated the successful application of the method in the presence of these interfering ions.

3.8. Analytical performance

The calibration curve for zinc for ICP-OES was given in supplementary Fig. S6. The analytical performance of the method was evaluated using key performance criteria, including the limit of detection (LOD) (LOD formula: 3Std/m) limit of quantification (LOQ) (LOQ formula: 10Std/m), relative standard deviation (RSD) (RSD formula: Std/Xort x100), and preconcentration factor (PF). The LOD-LOQ for liquid samples, LOD-LOQ for solid samples, and %RSD were calculated as 0.77 μg L^{-1}- 2.56 μg L^{-1}, 0.58–1.92 μg kg^{-1} and 3.9 %, respectively, based on the preconcentration factor derived from seven parallel blank measurements prepared using the NiO nanoflower-DμSPE method (Std: standard deviation, X_{ort}: average of five measurement results, m: slope). The re-use of the NiO nanoflowers was also assessed for cost-effectiveness and sustainability. Five extraction cycles were done with optimized the DμSPE method. Afterwards, recoveries have been diminished to % 87.

3.9. Applications

The analysis of certified reference material (CRM) for NiO nanoflower- DμSPE method was conducted to assess its accuracy in determining zinc concentrations using the NiO nanoflower-DμSPE method.

Table 2
Results of SRM analysis (pH: 7.0, n: 3, eluent volume: 3 mL, adsorbent amount: 20 mg, eluent concentration: 0.5 M).

SRM Sample	Measured (µg g^{-1})	Certified value (µg g^{-1})	Recovery, %
1573-a tomato leaves	30.2 ± 0.2	30.9 ± 0.7	97.8

Table 3
Analysis of real samples (pH: 7.0, n: 3, eluent volume: 3 mL, adsorbent amount: 20 mg, eluent concentration: 0.5 M).

Sample	Concentration (µg kg^{-1})
Strawberry	N.D.[a]
Cocoa	14.6 ± 3.1
Spinach	N.D.
Hazelnut	21.3 ± 4.2

[a] N.D.: Not Detected

For this purpose, 1573-a tomato leaves were selected as the CRM. Specifically, 1 g of 1573-a tomato leaves CRM was weighed, to which 9 mL of nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2) were added. The mixture was then subjected to microwave-assisted digestion to ensure complete dissolution. Following this preparation, the pH of the resulting CRM solution was adjusted to 7.0, and the outcomes obtained through the NiO nanoflower- DµSPE method are summarized in Table 2. The quantitative recovery values were obtained for certified reference material.

After optimizing the NiO nanoflower-DµSPE method, recovery studies were conducted by spiking mixed matrix media with known concentrations of analytes. Environmental water and wastewater samples were utilized to validate the method's accuracy. Initially, the water samples intended for analysis were filtered using a 0.45 µm cellulose membrane. Following this, addition/recovery studies were performed by incorporating increasing concentrations of a zinc stock solution. The prepared solutions were subsequently analyzed using ICP-OES to determine their zinc content. The results presented in Table S1 indicate that recoveries ranged from 90 % to 102 %, demonstrating the successful application of the method to real samples.

The developed NiO nanoflower-DµSPE method was employed for zinc preconcentration studies in food samples, including spinach, hazelnut, cocoa, and strawberry. The pH of these samples was adjusted to 7.0 using 1 mL of buffer solution prior to applying the NiO nanoflower-DµSPE method with 20 mg of NiO nanoflower. The analysis results obtained from ICP-OES are summarized in Table 3.

3.10. *A comparative overview of the DµSPE method against to various extraction techniques in the literature*

The separation and preconcentration of zinc from food and water samples using the developed NiO nanoflower-DµSPE method were compared with other extraction methods reported in the literature. As presented in Table 4, the limit of detection (LOD) and limit of quantification (LOQ) values obtained in this study are significantly lower than those found in other studies. Additionally, high recovery rates ranging from 90 % to 102 % were achieved, demonstrating the superior performance and effectiveness of the NiO nanoflower-DµSPE method in zinc extraction compared to existing methods.

4. Conclusions

In this study, the DµSPE method was investigated for the separation, preconcentration and determination of zinc from food and water samples using ICP-OES. After the parameters such as pH, extraction time and matrix effect were optimized, its application was performed on real-samples. Analyte addition studies were carried out to wastewater and tap water to prove the accuracy of the method. Furthermore, the method was successfully implemented to SRM and food samples. The optimized DµSPE procedure exhibits advantages such as simplicity, short extraction time, environmental friendliness, low acid concentration of solvent usage and unique extraction efficiency for zinc from food and water samples. On the contrary, this extraction method' s drawback is the use of appropriate filtration in case of clogging problem of capillary tubes during the measurement. What's more, the novel research holds great importance for environmental sustainability, as the facilely synthesized nanoflower particle may remove pollutants including heavy metals, pesticides, and, dyes in water samples.

CRediT authorship contribution statement

Basaran Erkan: Writing – original draft, Methodology, Investigation. **Erbilgin Duygu Erkmen:** Writing – original draft, Methodology, Investigation. **Beydagi Buse Bozan:** Writing – original draft, Methodology, Investigation. **Kizil Nebiye:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation. **Soylak Mustafa:** Writing – review & editing, Writing – original draft, Supervision. **Yola Mehmet Lütfi:** Writing – review & editing, Writing – original draft. **Uzcan Furkan:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Topaloğlu Dilek:** Writing – original draft,

Table 4
Comparison of NiO nanoflower-DµSPE method with other zinc microextraction studies in the literature.

Extraction Method	AnalyticalMethod	Amount of adsorbent	LOD[a]	PF[b]	Recovery, %	Sample	Ref.
Deep eutectic solvent-based liquid phase microextraction	FAAS	-	1.542 µg kg^{-1}	20	92.49–98.93	Milk, oil, fish	Elahi et al., 2022
Solid phase microextraction	AAS	60 mg	-	-	97.7–98.6	Meat, chicken	Vojoudi et al., 2018
Ultrasonic-assisted dispersive liquid-liquid microextraction based on solidification of floating organic drop	FAAS	-	1.8µg L^{-1}	20	96.0–100.0	Chicken, fish, tomato, apple, spinach	Mortada et al., 2024
Solid phase microextraction	FAAS	100 mg	12.30 µg L^{-1}	13.25	105	Nuts	Umaz et al., 2024
Cloud Point Extraction	UV-Visspectrophotometer	-	0.003 µg mL^{-1}	-	95.0–97.6	Water samples	Moustafa et al., 2023
Solid phase microextraction	FAAS	30 mg	0.001 µg mL^{-1}	100	97.1–105.0	Milk, potatoes, water samples, rice, tea	Roushani et al., 2015
Solid phase microextraction	ICP-OES	20 mg	0.77 µg L^{-1}	10	90.0–102.0	Tap water, wastewater, strawberries, cocoa, spinach	Current paper

[a] Limit of defection,

[b] Preconcentration factor

Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2025.107348.

Data availability

No data was used for the research described in the article.

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